



## Highlights (for review)

- The dynamics of UV-induced oxygen vacancy is studied from the change of surface resistance.
- The formation of 2DEG at the insulating surface of SrTiO<sub>3</sub> is confirmed by ARPES.
- The UV-induced change in resistance responds differently to oxygen/gas exposure.
- The behavior of resistance recovery suggests an alternative method of low-pressure sensing.

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# The dynamics of ultraviolet-induced oxygen vacancy at the surface of insulating SrTiO<sub>3</sub>(001)

S. Suwanwong,<sup>1,2</sup> T. Eknapakul,<sup>1</sup> Y. Rattanachai,<sup>3</sup> C. Masingboon,<sup>1,4</sup> S. Rattanasuporn,<sup>5</sup>  
R. Pattanakun,<sup>5</sup> H. Nakajima,<sup>5</sup> P.D.C. King,<sup>6</sup> S. K. Hodak,<sup>7</sup> and W. Meevasana<sup>1,8,9,\*</sup>

<sup>1</sup>*School of Physics, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand*

<sup>2</sup>*Program in General Science Teaching, Faculty of Education,*

*Vongchavalitkul University, Nakhon Ratchasima 30000, Thailand*

<sup>3</sup>*Department of Applied Physics, Faculty of Sciences and Liberal Arts,*

*Rajamangala University of Technology Isan, Nakhon Ratchasima 30000, Thailand*

<sup>4</sup>*Faculty of Science and Engineering, Kasetsart University,*

*Chalermphrakiat Sakon Nakhon Province Campus, Sakon Nakhon, 47000, Thailand*

<sup>5</sup>*Synchrotron Light Research Institute, Nakhon Ratchasima, 30000, Thailand*

<sup>6</sup>*SUPA, School of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife KY16 9SS, United Kingdom*

<sup>7</sup>*Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*

<sup>8</sup>*NANOTEC-SUT Center of Excellence on Advanced Functional Nanomaterials,*

*Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand*

<sup>9</sup>*Thailand Center of Excellence in Physics, CHE, Bangkok, 10400, Thailand*

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The effect of ultra-violet (UV) irradiation on the electronic structure and the surface resistance of an insulating SrTiO<sub>3</sub>(001) crystal is studied in this work. Upon UV irradiation, we show that the two-dimensional electron gas (2DEG) emerges at the insulating SrTiO<sub>3</sub> surface and there is a pronounced change in the surface resistance. By combining the observations of the change in valence band and the resistance change under different environments of gas pressure and gas species, we find that UV-induced oxygen vacancies at the surface play a major role in the resistance change. The dynamic of the resistance change at different oxygen pressures also suggests an alternative method of low-pressure sensing.

## I. INTRODUCTION

Since the discovery of a thin layer of two-dimensional electron gas (2DEG) at the interface between the insulating oxides LaAlO<sub>3</sub> and SrTiO<sub>3</sub> [1], a number of interesting properties at the oxide interfaces have been reported including superconductivity [2], large magnetoresistance [3], ferromagnetism [4] and electric-field-tuned metal-superconductor-insulator phase transitions [5]. These set a route to create novel devices with functionalities not available in conventional semiconducting ones. By using angle-resolved photoemission spectroscopy (ARPES), we also found that upon ultra-violet (UV) irradiation, two-dimensional electron gas can also occur on the bare surface of lightly-doped SrTiO<sub>3</sub>(001) without the oxide-oxide interface [6] while its charge density can be controlled via UV exposure. The electronic structure at this bare SrTiO<sub>3</sub> surface is also similar to another ARPES study [7] and the calculated one of the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface [8].

While it is possible to create the 2DEG state at the SrTiO<sub>3</sub> surface via other means (e.g. hydrogen exposure [9]), in this case, the 2DEG occurs due to oxygen vacancies induced by the UV irradiation [6, 10, 11]. These oxygen vacancies cause a narrow potential well near the surface and the quantized 2DEG states are the bounded

states in this quantum well. After the UV irradiation stops, the 2DEG states can still last very long time at least in order of hours in ultra-high-vacuum condition (e.g. at the base pressure of around 10<sup>-11</sup> mbar) [6]. However, ARPES technique is not suitable for studying the dynamics of these 2DEG states at the pressure higher than around 10<sup>-9</sup> mbar.

To study the dynamics of these oxygen vacancies at intermediate vacuum condition (e.g. around 10<sup>-8</sup> - 10<sup>-4</sup> mbar), in this letter, we performed experiments to measure the electrical resistance of the SrTiO<sub>3</sub> surface during and after the UV irradiation; as later shown, at this range of pressure, the recovery of the surface can also be observed much clearer. We note that the samples measured here are the undoped, insulating crystals, unlike in our previous study which uses lightly-doped sample; therefore, the effects observed here will get much less contribution from the bulk. To be certain, we also performed ARPES measurement to confirm the formation of the 2DEG states on these insulating samples.

## II. MATERIALS AND METHODS

SrTiO<sub>3</sub> samples measured in the work (Crystal Base Co., Japan) are undoped single crystals with (001) crystal orientation and 5 × 5 × 1 mm<sup>3</sup> in dimension. Using a Scienta R4000 hemispherical analyzer, the ARPES measurement of this set of samples was performed at beamline 10.0.1 of the Advanced Light Source to ensure the

\*Electronic address: worawat@g.sut.ac.th

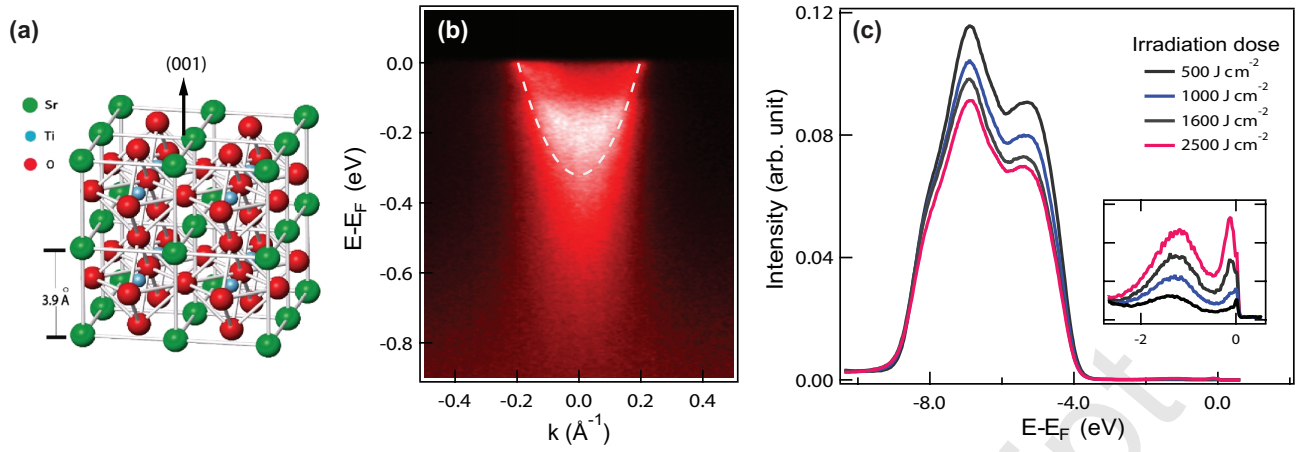


FIG. 1: (a) Atomic structure of SrTiO<sub>3</sub> crystal with (001) orientation. (b) Electronic structure of the 2DEG states at the UV-irradiated SrTiO<sub>3</sub> surface with dose of 2500 J cm<sup>-2</sup>; the dash line is the band dispersion guided by eye. (c) The change in the valence band of oxygen state ( $O_{2p}$ ) and the in-gap state (the zoomed-in graph is in the inset) upon UV irradiation.

formation of 2DEG under UV irradiation (see Fig. 1). The measurement temperature was done at 20 K and the photon energy was set to 55 eV; more details of the measurement are similar to the procedures used in Ref. [6] and [12].

For the resistance measurement under UV irradiation, the UV irradiation was from the synchrotron radiation in the zeroth order mode with the peak intensity around 60 eV; the estimated intensity is around 2.4 W/cm<sup>2</sup>. All the resistivity measurements at room temperature were performed at beamline 3.2a, Synchrotron Light Research Institute (SLRI). The gold electrodes on the surfaces of these SrTiO<sub>3</sub> crystals with the pattern as shown in the inset of Fig. 2 were made at SLRI beamline 6, by using sputtering technique; the smaller spacing between the two electrodes is 50 μm and the larger width is 2 mm. These samples were then cleaned with acetone and ethanol before putting on the sample holder in the ultra-high-vacuum (UHV) chamber. By using a sourcemeter (Agilent B29014), the resistances of these samples were then measured under various conditions of UV-irradiation doses and gas pressures as later stated.

### III. RESULTS AND DISCUSSION

Fig. 1(a) shows the ARPES data of 2DEG state at the surface of undoped SrTiO<sub>3</sub>. Initially, right after cleaving, the sample showed no 2DEG state as expected from an insulating undoped sample. To avoid the charging effect of the insulating sample during the UV irradiation, the beam spot was set to be in the position which overlaps between the sample and the electrical ground of the sample holder; this will allow electrons to flow from the ground to the area of the irradiated sample surface which become metallic. After intense UV irradiation, the 2DEG state started to emerge as shown in Fig. 1. Although the ARPES data is not as clear as in the case of using

lightly-doped sample [6], the 2DEG states are still clear enough to extract the surface density ( $n_{2D}$ ). From the observed Fermi surface areas, the extracted  $n_{2D}$  is least around  $9 \times 10^{13}$  cm<sup>-2</sup>. This surface density is already large comparing to most of conventional semiconductors [13], indicating that the change at the insulating surface is still quite pronounced. To observe the change at the surface, we also measured the valence band during the UV irradiation (see Fig. 1(b)). Upon increasing the irradiation dose, the oxygen ( $O_{2p}$ ) peak became smaller but the in-gap state with peak around 1.3 eV (see inset), which is associated with the oxygen vacancy [11, 14], became larger. This suggests that oxygen vacancies are created during the irradiation and the 2DEG state then starts to form inside the quantum well (i.e. the band bending at the surface) [6].

These 2DEG states are expected to contribute to the conductivity of the surface. To investigate on this, we set up a resistivity measurement with diagram shown in the inset of Fig. 2. The gold electrodes were fabricated in a zigzag pattern to increase the possibility of overlapping between the beam spot of the UV irradiation and the two electrodes; with this overlapping, the conductive 2DEG region created at the SrTiO<sub>3</sub> surface would well be connecting to the two electrodes and the electrons can flow between the two electrodes. As shown in Fig. 2, before the UV irradiation, the resistance of the SrTiO<sub>3</sub> sample at pressure of  $2 \times 10^{-8}$  mbar was observed to around 4 GΩ. When the UV irradiation was first on, the resistance dropped quickly to below 10 MΩ. Then, when the irradiation was off again, the resistance would increase back but at the much slower rate. The resistance still showed a trend of slow decrease during the continuing on-off process.

The features of this resistance change suggests the existence of at least a few effects occurring during the on-off process, including photoconductivity effect, creation of oxygen vacancy and surface recovery. When the light is

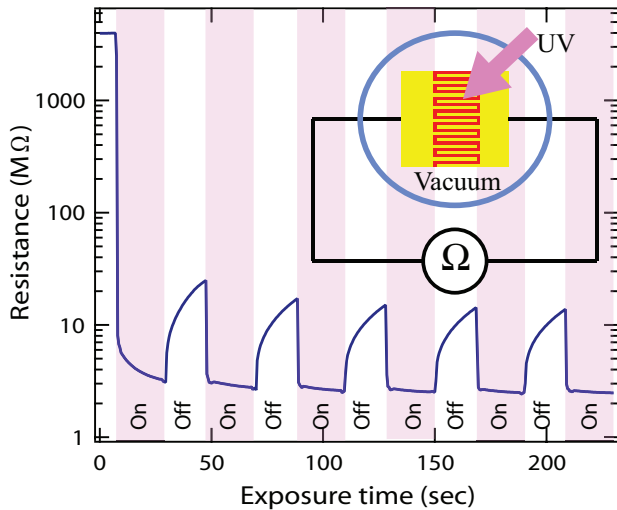


FIG. 2: The measured resistance of the SrTiO<sub>3</sub> surface where the on-off process of the UV irradiation is as indicated. The inset shows the schematic diagram of the measurement setup.

on, the photoconductivity is known to contribute to the change in resistance. This effect is relatively dynamic, i.e. it should occur and disappear quickly when the light is on and off respectively (e.g. the response time  $< 1$  ms even at low temperature in Ref. [15]). However, since the resistance measured here does not instantly recover back to its original value when the irradiation is off (i.e. still last for many seconds) or still keeps decreasing when the irradiation is on, the oxygen-vacancy-induced 2DEG state, which occurs at much larger time scale as shown in the ARPES data above, should also play a major role in these features of resistance change observed here. Note that the change in resistance under UV irradiation of titanium oxide compounds already finds various applications as previously reported, e.g. UV detector [16], light-sensitive capacitor [17–19] and enhanced magnetism [20].

In the oxygen-vacancy scenario, the resistance of an insulating sample will become lower when more of oxygen vacancy is created on the SrTiO<sub>3</sub> surface; on the other hand, if the vacancies are healed with oxygen exposure, the resistance should become higher again. To investigate on this, after stopping the UV irradiation at each time, we let the SrTiO<sub>3</sub> surface recover under different oxygen pressures between  $4 \times 10^{-8}$  to  $1 \times 10^{-4}$  mbar. As shown in Fig. 3(a), the sample resistance clearly responds to the oxygen exposure where the recovering rate is larger in the higher oxygen-pressure environment. Furthermore, we have performed a series of control experiments to substantiate the role of surface oxygen vacancies. As shown in Fig. 3(b), we find negligible change in the resistance upon exposure to Ar and N<sub>2</sub> as compared to oxygen at the same pressure. Together with the increasing recovery rates with increasing partial oxygen pressure, these experiments provide strong evidence for the oxygen-vacancy role in the observed resistance change

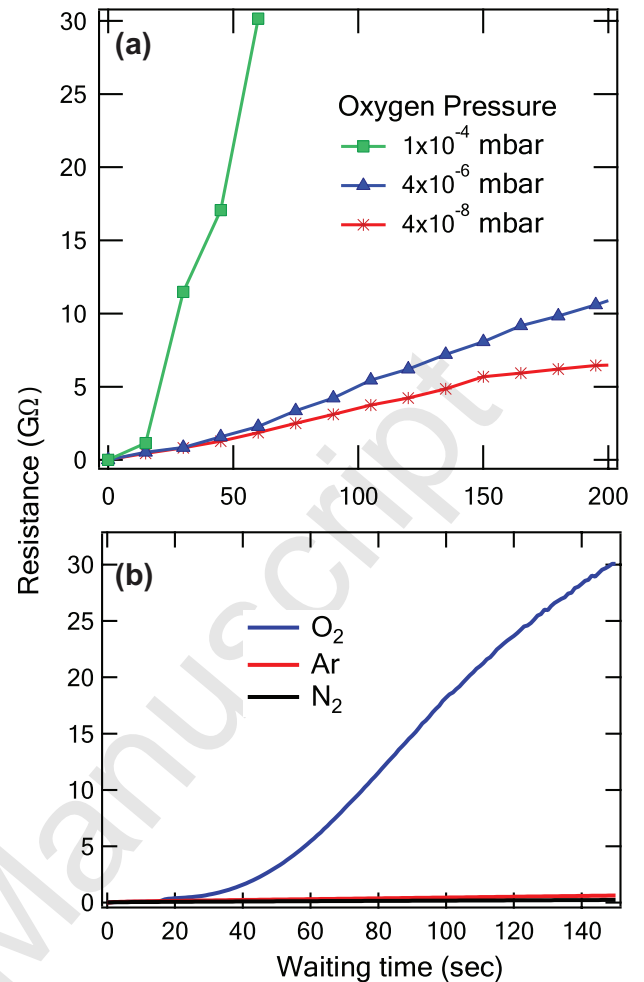


FIG. 3: (a) The recovering resistance of the SrTiO<sub>3</sub> surface at different oxygen pressures; before the measurement, the surface is irradiated with UV light in the same condition to have a similar starting resistance. (b) The comparison between the recovering resistance with the exposure to different gas species of the same pressure.

upon UV irradiation. This dynamic change may be useful information for the fabrication of the LaAlO<sub>3</sub>-SrTiO<sub>3</sub> interface as it is known that the oxygen partial pressure can affect the transport property at the interface [21]. Besides this, the effect shown in Fig. 3(a) suggests an alternative method to measure the oxygen pressure extracted from the recovering rate of the resistance; from the data, the pressure can at least cover in the range between  $10^{-8}$  –  $10^{-4}$  mbar. For each measurement using this method, the first UV irradiation is still needed. We find that a UV laser/flashlight (e.g. with wavelength of 385-405 nm, and intensity of around  $1 \text{ W/cm}^2$ ) may work well for this purpose; however, further investigation is required.

#### IV. SUMMARY

Our ARPES data confirm that the 2DEG states can occur on the insulating, undoped SrTiO<sub>3</sub>(001) after UV irradiation. The origin of these 2DEG states is the UV-induced oxygen vacancies as supported by both the corresponding valence band and the recovery nature after exposure to oxygen environment. For the resistance measurement, we observe clear reduction of surface resistance under UV irradiation where oxygen vacancies appear to play a major role. After UV irradiation, the active recovery process of surface resistance can be observed over a large time scale (e.g. in order of 10 sec at the oxygen partial pressure of  $10^{-8} - 10^{-4}$  mbar); with this, we

also suggest an alternative method to measure oxygen partial pressure from the clear difference in recovery rate observed here.

#### V. ACKNOWLEDGMENTS

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